January 20, 1898.

The LORD LISTER, F.R.C.S., D.C.L., President, in the Chair.

The Right Hon. Sir Nathaniel Lindley, Master of the Rolls, one of Her Majesty's Most Honourable Privy Council, was balloted for and elected a Fellow of the Society.

A List of the Presents received was laid on the table, and thanks ordered for them.

The following Papers were read:—

I. "The Relations between Marine Animal and Vegetable Life." By H. M. VERNON, M.A., M.B. Communicated by Professor J. BURDON SANDERSON, F.R.S.

II. "The Homogeneity of Helium." By WILLIAM RAMSAY, Ph.D., LL.D., Sc.D., F.R.S., and MORRIS W. TRAVERS, B.Sc.

III. "Fergusonite, an Endothermic Mineral." By WILLIAM RAMSAY, Ph.D., LL.D., Sc.D., F.R.S., and MORRIS W. TRAVERS, B.Sc.

IV. "On the Modification of the Spectra of Iron and other Substances, radiating in a strong Magnetic Field." By THOMAS PRESTON, M.A. Communicated by Professor G. F. FITZGERALD, F.R.S.

"The Homogeneity of Helium." By WILLIAM RAMSAY, Ph.D., LL.D., Sc.D., F.R.S., and MORRIS W. TRAVERS, B.Sc. Received December 2, 1897,—Read January 29, 1898.

About a year ago, a paper by Dr. Norman Collie and one of the authors (W. R.) was published, bearing the title "The Homogeneity of Helium and of Argon." In that paper* various reasons were adduced to show why an attempt to determine whether or no argon and helium are homogeneous was worth making. The results of the experiments at that time indicated that while it did not appear possible to separate argon into two portions of different densities, the case was different with helium. Samples were obtained after

* 'Roy. Soc. Proc.,' vol. 60, p. 206.

repeated diffusion which possessed respectively diffusion rates corresponding to the densities 2·133 and 1·874. It was there pointed out that these densities are not correct (although their ratio is probably not wrong), owing to the curious fact that the rate of diffusion of helium is too rapid for its density, *i.e.*, it does not follow Graham's law of the inverse square root of the densities. These samples of gas also differed in refractivity, and the difference was approximately proportional to the difference in density.

Towards the end of the paper, the conjecture was hazarded that it was not beyond the bounds of possibility that the systematic diffusion of what we are accustomed to regard as a homogeneous gas, for example, nitrogen, might conceivably sift light molecules from heavy molecules. It is true that the fineness of the lines of the spectrum would offer an argument in favour of the uniformity of molecular weight; but still it is never advisable to assume any physical theory without submitting it to rigorous proof. And it was thought possible that the fractional diffusion to which helium had been subjected might have had the result of effecting such a separation; a separation, not of chemical species, but of molecular magnitude. The other and more ordinary explanation of the splitting of helium into fractions of different density is that helium must be regarded as a mixture of two gases, one lighter than the other.

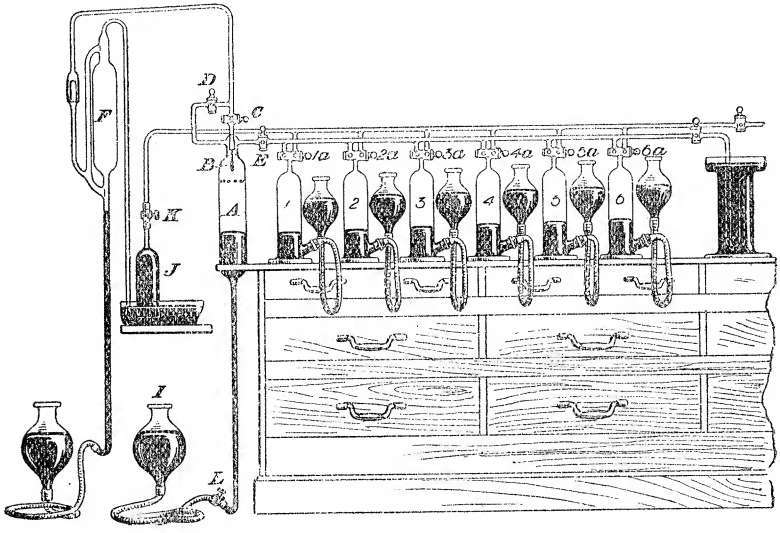
Since the publication of the paper mentioned, Dr. A. Hagenbach has confirmed the possibility of separating helium into portions of two densities by diffusion; and the differences in density were practically the same as those observed in the laboratory of University College.*

These experiments were made with somewhat over 200 c.c. of gas; but it was decided to make experiments of a similar kind, on a much larger quantity of helium.

An apparatus was therefore constructed, similar in principle to the one previously employed, but on a much larger scale. The main features are shown in the illustration on p. 208 of the paper previously alluded to; but on account of the large amount of gas diffused, it was not practicable to collect it in tubes. Instead, therefore, of the bent tube EN of the former apparatus, the tube connected with the stopcock E was continued horizontally, and by means of six vertical branches it communicated with six gas reservoirs, each furnished with a two-way stopcock. It was possible with this means to cause gas from any one of the reservoirs to enter the diffusion apparatus A. In order to be able to collect the gas in any desired reservoir, the delivery tube of the Töpler pump F delivered gas into a jar somewhat similar to that shown at J, but provided with a vertical branch, which was bent horizontally some

* 'Wied. Ann.,' vol. 60, p. 124.

distance up, and lay parallel to the previously mentioned horizontal tube. It, too, had six vertical branches, each of which communicated with the other limb of the two-way stopcock of each reservoir. By raising the reservoir of the Töpler pump and expelling gas into the collecting tube J, the gas could be transferred to any one of the reservoirs. The accompanying diagram makes it clear how the apparatus was set up.



The actual method of conducting a diffusion was as follows:—

Reservoir I was raised until the mercury in the diffusion jar A stood at the level of the dotted line. The clip L was then closed, and the stopcocks C and D opened. The Töpler pump was then worked until all gas was removed from A; the gas, if air (as at the commencement of the whole series of operations), being allowed to escape by moving the collecting jar J, so that it no longer covered the end of the exit tube of the Töpler pump. Stopcocks C and D were next closed, and stopcocks E and 6*a* opened, so that the gas from 6 entered the diffusion vessel A. By raising the reservoir belonging to 6, all gas was expelled through E into A, clip L being opened meanwhile. Reservoir 6 was now full of mercury, and all gas was in A. Stopcock C was then opened, and the gas in A diffused through the pipe stem B (closed at one end by means of an oxy-hydrogen blowpipe) into the pump. This diffusion proceeded until half the gas in A had passed into the pump reservoir F. Stopcock C was then closed, and the Töpler was worked, the diffused gas being delivered into J. Stopcock 6*a* was then opened, and the reservoir of

6 lowered, so that the gas in J passed into 6. This stopcock was then shut. The contents of 5 were then transferred in a similar manner into A, and one-third of the gas was diffused into the pump. It was collected as before in 6. The diffusion jar A now contained as much gas as had been present in 5. The contents of 4 were next added; half of this was removed by diffusion and transferred to 5. The contents of 3 were added; half was diffused and transferred to 4. The contents of 2 were added; half was diffused and collected in 3. And, lastly, the contents of 1 were added, and the half diffused collected in 2. Stopcock D was then opened, and the mercury in the diffusion jar A allowed to run up to the dotted line; the clip L was closed. All gas was pumped out of A and collected in 1; this constituted one complete round.

As it was not possible to empty the tube issuing from J completely of gas by lowering the reservoir of 1, and as, if not emptied, the heavy gas would have contaminated the light gas from 6 during the next round, the following method was made use of. The gas from 6 was transferred to the empty reservoir A; and then, by lowering the reservoir of 6, mercury rose in the tube issuing from J, and expelled all the heavy gas in the connecting tubes into 6. The clip K was then closed, and by opening the stopcocks 1*a* and 6*a*, so that communication took place between jars 1 and 6, the small quantity of gas in 6 was transferred to 1. The apparatus was now ready for a second round.

The Fractional Diffusion of Air.

In order to test the working of the apparatus, a set of diffusions was carried out with air. After four rounds, comprising twenty-four diffusions, the light portion contained 17·37 per cent. of oxygen and the heavy portion 22·03. A fairly rapid separation was thus being effected, considering the closeness of the densities of nitrogen and oxygen.

The Fractional Diffusion of Nitrogen.

A similar set of experiments was carried out with nitrogen, prepared by the action of solutions of ammonium chloride on sodium nitrite, in presence of copper sulphate. The gas was dried and passed over red-hot iron prepared by reduction of ferric oxide in order to remove any oxygen or to decompose any oxides of nitrogen which might be present. After thirty rounds, involving 180 operations, the "light" portion of the nitrogen, after purification by circulation over copper oxide, had not altered in density. It must therefore be concluded that nitrogen is homogeneous as regards the relative density of its individual molecules.

The Fractional Diffusion of Helium.

The first sample of helium employed was prepared from samarskite and cleveite. After seventeen rounds, involving 102 operations, the diffusion rates of the lighter and heavier portions were measured. The first gave a density, calculated from this rate, of 1·807, and the second of 2·128. The same gas was re-diffused until in all thirty rounds had been carried through, involving 180 operations. The light fraction now showed the density (measured diffusion rate against hydrogen) 1·816, and the heavy fraction 2·124. These gases were then circulated; the diffusion rate of the lighter portion pointed to a density of 1·811; the heavier gas was diffused into three portions, of which the more rapidly diffusing had a "diffusion density" of 1·906, and the less rapidly diffusing of 2·032. The lightest gas of all (diffusion density = 1·811) was weighed, and had a "real" density (O = 16) of 2·021; the mixture of the heavy products gave the real density, 2·153. The refractivity of the heavy portion, measured against helium from cleveite, undiffused, yet purified from all removable gases, which had the density (weighed) 2·076, was 1·078, the refractivity of the undiffused gas being taken as unity.

A fresh quantity of helium was next prepared from cleveite, and the former diffused samples were stored in tube-reservoirs for future use. The new helium was washed with caustic soda, but not otherwise purified. This gas was now put through fifteen rounds, comprising ninety operations, and the light portion in jar 6 was purified by circulation over magnesium and copper oxide. Its refractivity was 0·9752 of that of the uncirculated helium. Its density by weighing was 1·979. Owing to the cracking of the glass apparatus the main bulk of the specimen was lost. It may be here interesting to chronicle that the remaining portion was inhaled through the nose and mouth; it possessed neither smell nor taste.

The contents of No. 5 were therefore purified and weighed; its density was 2·049.

The contents of No. 1 were also purified by circulation, and had a gravimetric density of 2·245. It lost on circulation a considerable amount of nitrogen which was estimated as ammonia by treatment of the magnesium containing nitride with water. As we are certain that there was no entry of air in preparing the gas, the 34 c.c. of nitrogen must have been evolved from the mineral. It may have been occluded on the surface of the powdered mineral; it need not be remarked that before heating the mineral a nearly perfect vacuum was made in the tube, and that there was no leakage during the operations. We have previously found traces of nitrogen in gas prepared from cleveite; but not all specimens give off that gas. Supposing, however, to take the worst view, the nitrogen had been

derived from leakage of air, it would correspond to only 0·3 c.c. of argon.

The contents of jar No. 2 were also purified and weighed. During the purification hardly a trace of nitrogen was removed. The density was 2·209. We have thus:—

Jar No.	1	contains gas of density	.....	2·245
„	2	„	.....	2·209
„	6	„	.....	1·979

The light gas which had previously been stored in tubes was now mixed with the light gas from the second set of diffusions, and the mixture was re-diffused fifteen times, involving ninety operations. The density of the lightest portion of this helium was determined by weighing and found to be 1·988. The helium had, therefore, not been made sensibly lighter by re-diffusion. The mean of the two determinations may be taken as the true density of pure helium; it is 1·98. The refractivity of this sample measured against hydrogen and multiplied by the ratio between hydrogen and air, viz., 0·4564, gives 0·1238. This specimen of light helium of density 1·988 was placed in one of the refractivity tubes, and the lightest helium of the former preparation (density = 1·979) in the other. They had the same refractivity (1000 to 1004). The contents of No. 1, obtained from the mixture of light gases had the density 2·030, showing that only a little heavier material had been withdrawn.

The lighter fractions of helium were then sealed up in glass reservoirs and stored. The heavier portions were placed in the diffusion apparatus and submitted to methodical diffusion.

After fifteen rounds (ninety operations) the heaviest fraction had density 2·275, the lightest 2·08. The refractivity of the heaviest gas was next determined and found to be 0·1327. This gas examined in a Plücker's tube showed brilliantly pure helium lines, but along with these the reds and green groups of argon. Calculating from the density of this gas it should contain 1·63 per cent. of argon according to the equation $1{\cdot}961x+20y = 2{\cdot}275$. Calculating from the refractivity the percentage of argon should be 1·05, from the equation $1{\cdot}245x + 0{\cdot}9596y = 13{\cdot}33$. A mixture of 99 per cent. of the purest helium and 1 per cent. of argon was made, and it showed the argon spectrum with about the same or with somewhat less intensity than the heaviest gas. Finally, the heavy gas was diffused to the last dregs, so that only about 0·5 c.c. remained undiffused; and this small residue, transferred to a Plücker tube, showed the argon spectrum with only a trace of the spectrum of helium. The yellow line and the bright green line were visible, but feeble. This spectrum was compared with that of a mixture of argon with a trace of helium, and nearly the same appearance was to be seen. With

the jar in parallel and a spark gap interposed the blue spectrum of argon was equally distinct in both tubes; and, more important still, *there was no trace of any unknown line.* It appears, therefore, that helium contains no unknown gas, nor is it possible to separate it by diffusion into any two kinds of gas; all that can be said is that most minerals which evolve helium on heating also evolve argon in small quantity. This accounts for the difference in density observed in different samples of helium; and in one instance, viz., malacone, the amount of argon evolved on heating the mineral, though small, was much in excess of the helium, so far as could be judged by the spectrum.

In the light of the experiments of which an account has here been given, it is necessary to reconsider the deduction drawn by Professors Runge and Paschen from the complex nature of the spectrum of helium as regards its complex nature. Sir Norman Lockyer has already pronounced in favour of the supposition that helium is a mixture, chiefly on the ground that in the spectra of certain stars some, but not all, of the helium lines are observable. It appears to us that this may well be accounted for by the hypothesis that the differences of temperature and pressure in the stars might produce variations in the spectrum of helium. If a jar and spark gap be interposed while observing the visible spectrum of helium, a profound alteration is to be noticed. The yellow line D_3 is to be seen near the electrodes, and is faint in the capillary portion of the tube, and one of the red lines disappears. The change is not as remarkable as in the case of argon, but is quite distinct and characteristic. Then, as before remarked, the green line becomes relatively stronger at low pressures, so that the light evolved in the tube is no longer the usual brilliant yellow, but dull greenish-purple. Is it not likely that the conditions obtaining in the stars may account for the absence of some of the lines ordinarily visible?

If the hypothesis of Runge and Paschen is correct, then the two gases to which they attribute the complex spectrum of helium must have nearly the same density. It has already been shown that by means of the apparatus used for the fractional diffusion of gases it is possible to effect a fair separation of the constituents of air after a few rounds. If the supposed constituents of helium differ in density in as high a proportion as 14 to 16, it is certain that some separation would have been effected. As there has been no such separation, the legitimate inference is that the density of the two supposed constituents does not differ by so great an amount, or that their existence is imaginary. It appears to us that too little is known regarding the nature of the vibrations which cause spectra to make it legitimate to theorise on the subject. It is surely conceivable that an atom may possess such a structure as to render it capable of propagating two

different sets of vibrations, each complete in itself, and each resembling the other in general form. Yet it must be acknowledged that our experiments have not disproved the existence of two gases in helium of approximately the same density; in fact it may be contended that helium is a pair of elements like nickel and cobalt.

We are disappointed in the result of this long research, because we had thought it not improbable that an element of density 10 and atomic weight 20 might prove to be the cause of the fact that different samples of helium possess different densities, according to the mineral from which they are extracted, and also of the separation of helium into portions of different densities by diffusion. We still regard it as by no means improbable that further research will lead to the discovery of the "missing" element, and this appears to be a fitting opportunity of stating our reasons for the belief.

The difference between the atomic weights of helium and argon is 40—4 = 36. Now, there are several cases of such a difference. If we compare the groups of which the first members are fluorine, oxygen, nitrogen, carbon, boron, beryllium, and lithium, we obtain the following table:—

	At. wt.			At. wt.	
Fluorine.....	19·0	16·5	Boron	11·0	16·0
Chlorine.....	35·5	19·5	Aluminium	27·0	17·1
Manganese.....	55·0		Scandium	44·1	
Oxygen	16·0	16·0	Beryllium	9·1	15·2
Sulphur.....	32·0	20·3	Magnesium	24·3	15·8
Chromium.....	52·3		Calcium	40·1	
Nitrogen	14·0	17·0	Lithium.....	7·0	16·0
Phosphorus	31·0	20·4	Sodium	23·0	16·1
Vanadium.....	51·4		Potassium.....	39·1	
Carbon	13·0	16·3	Helium	4·0	16·0
Silicon.....	28·3	19·8	?	20·0	20·0
Titanium	48·1		Argon.....	40·0	

The elements helium and argon have been given a provisional place.

The differences between the extreme members of these small groups are given in the short table which follows:—

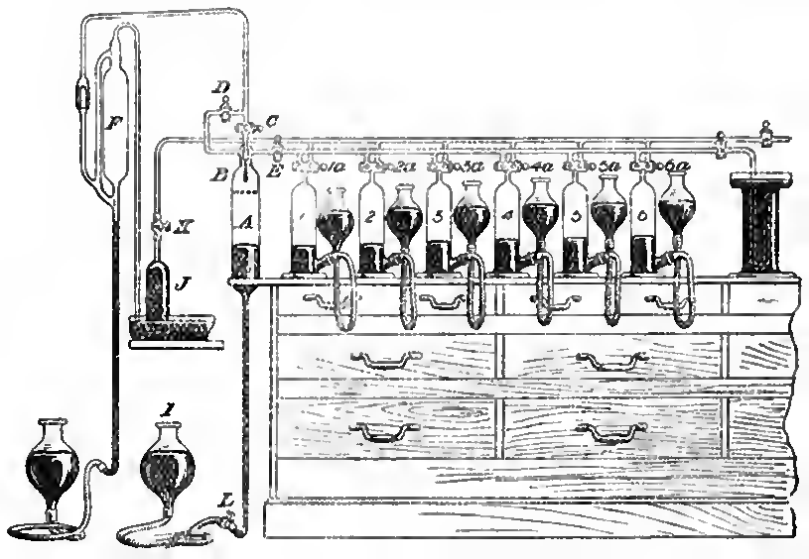
Manganese—Fluorine	36·0	Chromium—Oxygen	36·3
Vanadium—Nitrogen	37·4	Titanium—Carbon	36·1
Scandium—Boron	33·1	Calcium—Beryllium	31·0
Potassium—Lithium	33·1	Argon—Helium	36·0

The difference between the atomic weights of argon and helium, it

will be seen, is not far removed from those of the other pairs of elements. It appears, therefore, not improbable that there should be an element with atomic weight 20, resembling both argon and helium in its properties. Yet it is not so certain that the middle element should resemble argon and helium, for in the table given it is seen that there are several examples of elements with a middle place which do not resemble those at the extremes. The question is perhaps best left open.

It will be remembered that the gases evolved from a great many minerals and mineral waters have been examined, and that in many cases they have been found to contain helium and argon. In no instance up to the present has any sample of the gases evolved on heating in vacuum been found to show unknown spectrum lines. The amount of argon, as proved by the account which we have just given of our experiments, is very small, and in the case of the gas from cleveite investigated by Langlet it is probable that argon was almost completely absent, for it possessed the density 2. In malacone, on the contrary, argon is present in larger amount than helium, although neither gas is obtainable from it in large quantity. It appears to us not beyond the limit of probability that in some as yet uninvestigated mineral the middle member of the helium group may be discovered. When it is considered that germanium, an element which has been recognised only in one of the rarest of minerals, argyrodite, is the middle element of the trio, silicon, germanium, and tin, of which the first and last members are common, it is surely not unreasonable to hope that the middle member of the helium trio may ultimately be found. The amount of helium in fergusonite, one of the minerals which yields it in fair quantity, is only 33 parts by weight in 100,000 of the mineral, and it is not improbable that some other mineral may contain the missing gas in still more minute proportion. If, however, it is accompanied in its still undiscovered sources by argon and helium, it will probably be a work of extreme difficulty to effect its separation from these gases.

Addendum.—Since this paper was written, Professors Runge and Paschen, in a communication to the British Association in August of this year, have withdrawn their contention that helium is a mixture, or, perhaps more correctly stated, they now ascribe to helium the same complexity as that of oxygen, the spectrum of which may also be arranged in two series, each consisting of three sets of lines. As oxygen has not yet proved to be complex, the surmise that helium is complex therefore falls to the ground.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